Semiclassical S-matrix theory. VI. Integral expression and transformation of conventional coordinates*

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Sometimes, as in reactive systems, action-angle variables are not conveniently defined at all points of the trajectory and recourse must be made to conventional coordinates. A simple canonical transformation converts the latter to coordinates of which one is time and the remainder are constant along the trajectory. The transformation serves to remove the singularities of the semiclassical wavefunction at the turning points of the trajectory. It yields, thereby, an integral expression for the S matrix by having produced wavefunctions which can be integrated over all space. The result supplements that of Paper III [R. A. Marcus, J. Chem. Phys. **56**, 311 (1972)], which was derived for systems for which action-angle variables could be defined throughout the collision.

I. INTRODUCTION

Several derivations of a semiclassical expression for the S matrix are available, of different degrees of length and rigor.[1,2] (Other related semiclassical studies are given in Ref. 3.) Because of the many papers which are now appearing utilizing the method,[1,2,4] it is useful to review briefly the existing derivations and to generalize where needed.

In Sec. II we summarize a quick and intuitive derivation, using either the wavefunction[1] or the Feynman propagator[2] as a starting point. A limitation of such a derivation is pointed out: While it does lead to the correct stationary phase and uniform expression, it does not, without "fudging,"[2b] lead to a valid integral expression. The desirability of having an integral expression for S_{mn} is particularly true for systems for which the value of the integral does not arise almost exclusively from small neighborhoods of the stationary phase points of the integrand.[5]

Another derivation proceeds with more rigor from the standard expression for the S matrix[1b]:

$$S_{mn}\delta(E'-E)=\lim_{\substack{t_2\to+\infty\\ t_1\to-\infty}}\langle mE'|U_I(t_2,t_1)|nE\rangle = \langle mE'^{(-)}|nE^{(+)}\rangle, \tag{1.1}$$

where U_I is the evolution operator of the system in the interaction representation and where the second equality in (1.1) arises when one introduces the appropriate definition of the limits $t_2\to+\infty$ and $t_1\to-\infty$. The state vector $|mE'^{(-)}\rangle$ describes the state which is time reversed from $|mE'^{(+)}\rangle$. Equation (1.1) was first used in Paper III to derive an integral expression for S_{mn} for systems for which one can define action-angle variables for the internal coordinates *throughout the collision*. In the present paper we treat systems for which such a definition has either not been possible or not convenient.

We note that Eq. (1.1) is not in itself an integral (it is merely a scalar product), but when a coordinate representation of the vectors $|nE^{(+)}\rangle$ and $|mE'^{(-)}\rangle$ is used, it can be evaluated as one:

$$\langle mE'^{(-)}|nE^{(+)}\rangle=\int\langle mE'^{(-)}|\mathbf{Q}\rangle\,d\mathbf{Q}\,\langle\mathbf{Q}|nE^{(+)}\rangle, \tag{1.2}$$

where $\mathbf{Q}$ denotes the coordinates used. However, to evaluate this integral numerically it is necessary to use wavefunctions $\langle\mathbf{Q}|nE^{(+)}\rangle$ and $\langle\mathbf{Q}|mE'^{(-)}\rangle$ which are reasonably accurate over all space. When $\mathbf{Q}$ consists of a radial coordinate and internal coordinates, the semiclassical forms of the wavefunctions $\langle\mathbf{Q}|nE^{(+)}\rangle$ and $\langle\mathbf{Q}|mE'^{(-)}\rangle$ break down badly in certain regions and so may not be used for numerical evaluation of the integral in (1.2). [Such coordinates can typically still be used in (1.2) when (1.2) is evaluated by a stationary phase or related method, wherein essentially all of the value of the integral is contributed from certain very small regions of $\mathbf{Q}$ space.]

This breakdown of these semiclassical wavefunctions is well known, and occurs at "caustics." The latter consist of points or surfaces where neighboring classical trajectories propagating the semiclassical wavefunction intersect. An example of this intersection has been given by Wong and Marcus[1]: There, it was seen that the neighboring trajectories corresponding to final states of the collision system with neighboring (but different) final quantum numbers crossed at large (and at small) separation distances. (This crossing occurs always, in fact, after every inelastic or reactive collision.) The crossing itself gives rise to a singularity in the wavefunction because of conservation of probability flux: The perpendicular "distance" between neighboring trajectories (in

higher dimensions the "cross-sectional area") multiplied by the square of the local amplitude of the wavefunction and by the local velocity normal to that cross section yields the local flux. When the cross-sectional area of a bundle of trajectories vanishes, e.g., when there is an intersection of the trajectories, the amplitude of the semiclassical wavefunction must become infinite to conserve probability flux. In summary, the semiclassical wave function becomes singular where adjacent trajectories cross.

Thus, to evaluate the integral in (1.2) numerically it is necessary to use a different set of coordinates **Q** than the radial and internal coordinates. Another set of coordinates **Q** is the following: a point moving along a trajectory can be described by coordinates all but one of which are constants of the motion and the remaining one of which is time (or time plus a constant). In such a coordinate space the neighboring postcollision trajectories cannot actually cross each other at large separation distances, the previously mentioned singularity at large separation distances has thus disappeared, and the coordinate representatives $\langle \mathbf{Q} \mid nE^{(+)} \rangle$ and $\langle \mathbf{Q} \mid mE'^{(-)} \rangle$ become more suitable for use in a numerical evaluation of (1.2). The better the choice of the transformation to the new **Q**'s, in the sense of the accuracy of the new semiclassical wavefunctions, the more accurate will be the resulting numerical evaluation of (1.2) using those wavefunctions. In systems where the new final constants of the motion pass through an extremum, when one goes from a particular trajectory to a neighboring one, one again has a type of "crossing of trajectories" (an overlap of adjacent trajectories) and consequently less accuracy in the numerical evaluation of (1.2). Numerical examples of these cases will be given in a later paper.

The transformation to a new set of coordinates of which all but one are constants of the motion and the remaining one is time was employed in Paper III. There, angle coordinates were used for the internal degrees of freedom instead of, as now, conventional coordinates, as a starting point.

In Sec. III we first recall the semiclassical wavefunction expressed in terms of conventional coordinates. The use of such coordinates leads to the presence of a number of terms in the wavefunctions, in fact, typically 2^s terms for a system of s coordinates. The terms contain their usual singularities at turning-point surfaces (caustics). A simple and previously known canonical transformation is given in Sec. IV. It leads to new variables, of which one is time τ and the others are constants of the motion $\bar{w}_i$ for each trajectory. By removing the usual singularities this transformation also simplifies the semiclassical wavefunction, which becomes only one term.

The time-reversed wavefunction is given in Sec. V and is transformed there into one expressed as a function of $\bar{w}$ and τ. Equations (1.1) and (1.2) then lead to an integral over $\bar{w}$ and τ, given in Sec. VI. The τ integration cancels the δ function in (1.1) and gives the integral expression for S_{mn}. The result is the same as that in Paper III.

In two respects the present derivation is more straightforward than that in Paper III, the extra terms present in the original semiclassical wavefunctions notwithstanding. Obtaining the present time-reversed wavefunction is significantly simpler than that in Paper III: In the latter, one had to time reverse the action-angle variables and there are two different kinds of action-angle variables with different time-reversal behavior. Now, one simply changes the sign of all momenta. Secondly, Paper III tacitly involved two canonical transformations, one from conventional to action-angle coordinates and a second from the latter to $\bar{w}$ and τ. Now, a single and well-known transformation suffices.

II. HEURISTIC DERIVATION FOR THE SEMICLASSICAL $S_{n_2 n_1}$

To illustrate some features of the derivation in Sec. III it is useful to consider first a "quick" derivation which assumes that the S-matrix element for a transition for state n_1 to n_2, $S_{n_2 n_1}$, can be written as a matrix element $\langle n_2 E^0 \mid n_1 E^{(+)} \rangle$ and which also uses action-angle variables for the internal coordinates; n_1 denotes the quantum numbers of the system at some time t_1 before the collision ($t_1 \to -\infty$) and n_2 denotes those at some time t_2 after the collision ($t_2 \to +\infty$). The superscript (+) indicates a state which evolves during the collision and the corresponding collisional wavefunction is denoted by $\langle \mathbf{q} \mid n_1 E^{(+)} \rangle$. $\langle \mathbf{q} \mid n_2 E^0 \rangle$ denotes an unperturbed wavefunction. The totality of coordinates are denoted by $\mathbf{q}$, which in turn denotes, at large R, the radial coordinate R and the angle coordinates, the latter denoted collectively by q.

We have, by this argument,

$$S_{n_2 n_1} = \langle n_2 E^0 \mid n_1 E^{(+)} \rangle = \int \langle n_2 E^0 \mid \mathbf{q}_2 \rangle \, dq_2 \langle \mathbf{q}_2 \mid n_1 E^{(+)} \rangle , \tag{2.1}$$

where the integration over dq_2 is performed at a fixed final large value of R, R_2, and hence where the integration volume is written as dq_2 instead of $d\mathbf{q}_2$. The semiclassical wavefunction $\langle \mathbf{q}_2 \mid n_1 E^{(+)} \rangle$ is written as $A \exp i F_2(\mathbf{q}_2, N_1 E)$ (in units of $\hbar = 1$), where F_2 is a solution of the Hamilton–Jacobi equation:

$$H(\mathbf{q}, \partial F_2 / \partial \mathbf{q}) = E. \tag{2.2}$$

Here, $\partial F_2/\partial \mathbf{q}$ has been written for the momentum $\mathbf{p}$. Thereby, along a trajectory during the collision we have, in the present variables,

$$F_2(\mathbf{q}_2, nE) = \int_{q_1}^{q_2} \mathbf{p}\, d\mathbf{q} + \mathbf{p}_1\mathbf{q}_1 \tag{2.3}$$

A sum over all coordinates is intended in (2.3), but $\mathbf{p}d\mathbf{q}$ and $\mathbf{pq}$ are used for notational brevity.

The unperturbed wavefunction $\langle \mathbf{q}_2 \mid n_2E^0\rangle$ is $A_2^0 \exp iF_2^0(\mathbf{q}_2, n_2E)$, where F_2^0 satisfies the Hamilton–Jacobi equation at $t_2 = +\infty$:

$$H_0(\mathbf{q}, \partial F_2^0/\partial \mathbf{q}) = E, \tag{2.4}$$

H_0 being the Hamiltonian for the isolated particles. Thereby, in the present variables,

$$F_2^0(\mathbf{q}_2, n_2E) = \mathbf{p}_2\mathbf{q}_2 . \tag{2.5}$$

One finds, after stationary phasing (2.1),

$$S_{n_2n_1} = \langle n_2E^0 \mid n_1E^{(+)}\rangle = \left| i\partial^2F_4/\partial n_1\,\partial n_2 \right|^{1/2} \times \exp iF_4(n_2E, n_1E), \tag{2.6}$$

where

$$F_4(n_2E, n_1E) = \int_{q_1}^{q_2} \mathbf{p}\, d\mathbf{q} + \mathbf{p}_1\mathbf{q}_1 - \mathbf{p}_2\mathbf{q}_2 = -\int_{p_1}^{p_2} \mathbf{q}\, d\mathbf{p} . \tag{2.7}$$

The pre-exponential factor in (2.6) is chosen so as to make the S matrix unitary. The stationary phasing of the integrand in (2.1), plus introduction of the values for $\langle \mathbf{q}_2 \mid n_2E^0\rangle$ and $\langle \mathbf{q}_2 \mid n_1E^{(+)}\rangle$, ensure that the $\mathbf{q}_2$ in (1.2) satisfies the condition that $\partial(F_2 - F_2^0)/\partial \mathbf{q}_2 = 0$ and hence that the $\mathbf{p}_2$'s in F_2 and F_2^0 are matched.

The above derivation of (2.6) for $S_{n_2n_1}$ is, on the pro side, quick and, on the con side, oversimplified. As already noted it does not, without fudging, yield a valid integral for $S_{n_2n_1}$. This shortcoming stems in part from (a) the use of, in the integral (2.1), an expression for $\langle q_2 \mid n_1E^{(+)}\rangle$ for all q_2 which is not everywhere valid (the pre-exponential factor A becomes very inaccurate at certain intervals of q_2) and (b) from using $\langle n_2E^0 \mid n_1E^{(+)}\rangle$ instead of Eq. (1.1) for $S_{n_2n_1}$.

Similar comments apply to an analogous derivation based on the Feynman propagator,[2] which we recall here to emphasize the points noted earlier. Here, one recognizes that the S matrix is given by the first half of (1.1) but, in a quick derivation, neglects the δ function and hence neglects the difference between E and E' in the second half of (1.1).[2] Thereby one writes[2]

$$\begin{aligned} S_{n_2n_1} &= \langle n_2E^0 \mid e^{iH_0t_2}e^{-iH(t_2-t_1)}e^{-iH_0t_1} \mid n_1E^0\rangle \\ &= e^{iE(t_2-t_1)}\langle n_2E^0 \mid e^{-iH(t_2-t_1)} \mid n_1E^0\rangle \\ &= e^{iE(t_2-t_1)}\int\int \langle n_2E^0 \mid \mathbf{q}_2\rangle d\mathbf{q}_2 \langle \mathbf{q}_2 \mid e^{-iH(t_2-t_1)} \mid \mathbf{q}_1\rangle \\ &\quad \times d\mathbf{q}_1 \langle \mathbf{q}_1 \mid n_1E^0\rangle . \end{aligned} \tag{2.8}$$

The integrations are performed at a large fixed R_1 and R_2 (initial and final R) and hence dq_2 and dq_1 are used instead of $d\mathbf{q}_2$ and $d\mathbf{q}_1$.

The semiclassical form of the Feynman propagator can, apart from a normalization constant, be shown to be[6]

$$\langle \mathbf{q}_2 \mid e^{-iH(t_2-t_1)} \mid \mathbf{q}_1\rangle \sim e^{iS(q_2,q_1)}, \tag{2.9}$$

where S is the integral of the Lagrangian L:

$$S = \int_{t_1}^{t_2} L(\mathbf{q}, \dot{\mathbf{q}}, t)\, dt. \tag{2.10}$$

Since L equals $p\dot{q} - H$, one obtains from the last three equations, apart from a normalization constant,

$$S_{n_2n_1} \sim \int\int \langle n_2E^0 \mid \mathbf{q}_2\rangle\, dq_2 \times \exp\Big(i\int_{q_1}^{q_2} \mathbf{p}\, d\mathbf{q}\Big) dq_1 \langle \mathbf{q}_1 \mid n_1E^0\rangle, \tag{2.11}$$

where, as in (2.1), the integration is again performed at a fixed large R. Since $\langle \mathbf{q}_1 \mid n_1E^0\rangle$ equals $A_1^0 \exp i\mathbf{p}_1\mathbf{q}_1$ and $\langle \mathbf{q}_2 \mid n_2E^0\rangle$ equals $A_2^0 \exp i\mathbf{p}_2\mathbf{q}_2$, Eq. (2.11) again yields (2.6) and (2.7) after stationary phasing and normalization.

This derivation is seen to have much in common with the one leading from (2.1) to (2.7): Both yield the same integral expression, one which requires heuristic argument[2b] to introduce new variables $\overline{w}$ and hence to obtain a useful integral expression. The neglect of the (E, E') subtleties in (2.8) had, as their counterpart in (2.1) to (2.7), the use of $\langle n_2E^0 \mid n_1E^{(+)}\rangle$ instead of $\langle n_2E'^{(-)} \mid n_1E^{(+)}\rangle$. Finally, and in effect summarizing those shortcomings, the integrand in (2.1) and (2.11) has singularities which can only be legitimately removed (or reduced) by a suitable canonical transformation at the very outset in Eq. (1.1) itself. This step was done in Paper III and now, with conventional coordinates, in Sec. III.

One other shortcoming of (2.1)–(2.11), more minor, is that a certain term, $\exp[i(l_{n_1}+l_{n_2}+1)\pi/2]$, is missing in both (2.7) and (2.11); the l's are orbital quantum numbers. Actually, in Papers I and II a more careful starting point was used instead of the somewhat quicker (2.1)–(2.7) and this extra term was obtained.[1a] The method for including these terms when the Feynman propagator is used does not appear to have been explicitly given.

A third but minor defect lies in the appearance of certain fractional terms in the phase (2.3). Action variables J are related to quantum numbers n by the relation $J = (n + \delta)h$ or, in units of $\hbar = 1$, $2\pi(n + \delta)$; the δ depends on the particular degree of freedom; its value is known and is usually 0 or $\frac{1}{2}$. These J's and their canonically conjugate angle

coordinates w are used as the p's and q's for the internal coordinates in the quick derivation (2.1)–(2.11). One obtains, thereby, an extra $\frac{1}{2}w$ term in the phase (2.3) of the wavefunction $\exp ip_2q_2$, i.e., in $\exp[2\pi i(n+\frac{1}{2})w]$. The $\frac{1}{2}w$ terms violate single valuedness of the wavefunction. They can be avoided by more careful argument.[1] To be sure, they have no effect on the final outcome (2.7), but they should not be there at any stage.

In passing we note for further use that not only are the $2\pi(n+\delta)$ and w canonically conjugate and so satisfy $\{2\pi(n_i+\delta_i), w_j\}=\delta_{ij}$, where $\{\ ,\ \}$ denotes Poisson brackets, but also $2\pi n_i$ and w_i are canonically conjugate since $\{2\pi n_i, w_j\}=\delta_{ij}$.

III. SEMICLASSICAL WAVEFUNCTION WITH CONVENTIONAL COORDINATES

When one uses action-angle variables for the internal motions and a radial coordinate for the remaining degree of freedom, the semiclassical wavefunction for a collision typically consists of only two terms,[1] one for the ingoing motion and the other for the outgoing motion. This feature is one of the major simplifications afforded by use of action-angle coordinates; when instead conventional coordinates are used for a system consisting of internal coordinates and a radial coordinate, s coordinates in all, the semiclassical wavefunction is, as already noted, typically the sum of 2^s terms. In the present section we shall illustrate the present transformation for simplicity for the case of $s=2$, but the final results are generalized to any value of s in Sec. VI. The case of $s=2$ corresponds typically to a colinear collision of three particles (in the center-of-mass system of coordinates).

At large separation distances R the convenient coordinates are the radial coordinate R and internal coordinates, including (when s is greater than two) polar coordinates of the line of centers of the collision partners. When the internal coordinates are denoted collectively by q and the totality of all coordinates are again denoted by q, we have

$$\mathrm{q}\equiv(q,R) \text{ at large } R. \tag{3.1}$$

We shall need the phase integral to calculate the semiclassical wavefunction at any point. Inasmuch as the phase integral $\int p\,dq+\int p_R\,dR$ between any two points is invariant to a *coordinate* transformation, we may write it as $\int \mathrm{p}\,d\mathrm{q}$, without necessarily specifying the coordinates used to actually perform the integration. In practice, one frequently uses conventional coordinates (e.g., spherical polar, and vibrational). The end point of the trajectory used to calculate the phase integral will lie either in a reactants' or a products' channel. The final internal coordinates and radial coordinate may be that of reactants or of products, therefore. We need not specify which at this point.

Each term of the semiclassical wavefunction is of the form $A\exp iF_2(\mathrm{q}, nE)$, F_2 satisfying Eq. (2.2) of Sec. II, where the q now denotes conventional coordinates. [The n in (1.1), denoted by n_1 in (2.1), is again used.] The fact that there are many such terms in the semiclassical wavefunction reflects the multivaluedness of the function F_2. At any given point q each branch of F_2 involves a particular choice of initial signs of the various momenta in p. For example, Fig. 1 gives a sketch of some ingoing trajectories, each differing in vibrational phase at any given R and each having a negative radial momentum p_R. On branch II the vibrational component of momentum points toward the lower dotted line, while on branch IV it points away from that line, at the indicated value of R. Each dotted line is the locus of intersection of neighboring trajectories and serves as the locus of turning points of the vibrational motion. There-

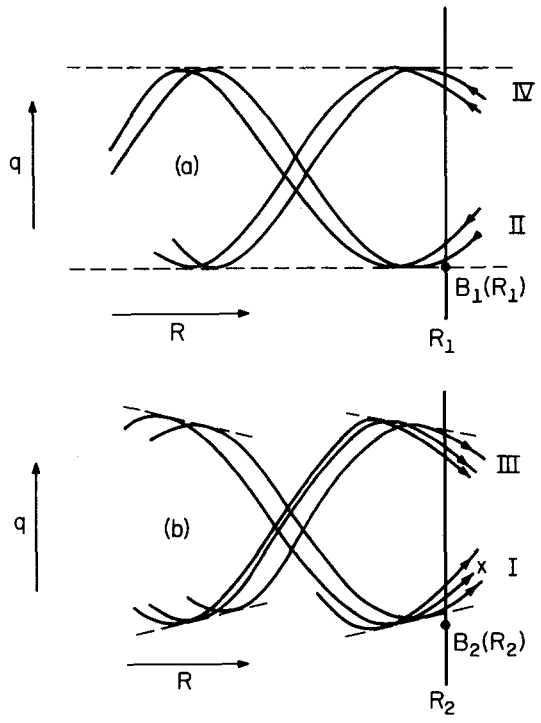

FIG. 1. Sketch of trajectories in (a) an entrance channel, indicating some contributing to branch F_2^{II} of F_2 and some contributing to F_2^{IV}, and (b) an exit channel, the two branches of F_2 being F_2^{I} and F_2^{III}. The dotted lines denote caustics. $B_2(R_2)$ differs for each trajectory since the final n, n_2, varies for each. $B_2(R_2)$ is the point where, for any given R_2, the p_γ for an isolated internal motion having that n_2 would vanish [cf. (4.4)]. The B_2 in Fig. 1(b) is the one appropriate for the middle trajectory (labeled x).

by, the upper and lower dotted lines will be referred to as the "outer" and "inner" vibrational turning points, respectively.

A quantum state of the collision pair as a whole is described semiclassically by an ensemble of such trajectories, each trajectory differing in initial vibrational phase. In Fig. 1 some trajectories lie on branch II while the others lie on branch IV, the former being used to construct branch F_2^{II} of F_2 and the latter to construct F_2^{IV}. An unperturbed wavefunction at any large value of R for this case of $s=2$ has a phase $(\int_{B_1}^{q} p_\gamma dq - k_n R)$, plus a constant $(\pm\pi/4$, as noted later) determined from the usual connection formula at the turning point. γ denotes the branch II or IV. p_γ is the vibrational momentum, the integration being at the specified R and from the vibrational turning point B_1 to q.

The phase integrals needed for the phase of any term (γ) of the semiclassical wavefunction at arbitrary q are composed of two parts:

$$\int_{B_1(R_1)}^{\mathbf{q}} \mathbf{P}_\gamma \, d\mathbf{q} \equiv \int_{B_1(R_1)}^{q_1(R_1)} p_\gamma dq + \int_{q_1}^{\mathbf{q}} \mathrm{p}_\gamma \, d\mathbf{q} \,, \qquad (3.2)$$

where $q_1[\equiv (q_1, R_1)]$ denotes the initial point on the trajectory at R_1, a large R in the entrance channel and outside the region of interaction of the collision partners. At the given R_1, the initial conditions are chosen to conform with the given initial state[1,2] and one chooses the initial q_1 so that the trajectory passes through the desired point q. The integral from $B_1(R_1)$ to $q_1(R_1)$ is an integration at fixed R, R_1, from the lower vibrational turning point B_1 to q_1. The integral uses the appropriate sign of p_γ for the branch γ. The integral from $\mathbf{q}_1$ to q in (3.2) is along the dynamical trajectory from $\mathbf{q}_1$ to q.

The phase of each term of the semiclassical wavefunction at q relative to that at $\mathbf{q}_1$ must also take cognizance of the number of times N_i, the trajectory between $\mathbf{q}_1$ and q, touches the dotted lines in Fig. 1 (the caustics, i.e., the lines formed by joining the turning points). Each time the trajectory touches such a line the term suffers a phase loss[6] of $\frac{1}{2}\pi$. We allow for this below.

Normalized to unit radial flux and to $\delta(n-n')$ or equivalently[7] to $2\pi\delta(E-E')\delta(n-n')$, the ingoing wavefunction is

$$\psi_i(\mathbf{q}, nE) = 2^{-1/2} \sum_{\gamma=\mathrm{II,IV}} \left| \partial^2 F_2^\gamma / \partial \mathbf{q} \, \partial \mathbf{P}_n \right|^{1/2} \times \exp[i(F_2^\gamma \pm \tfrac{1}{4}\pi - \tfrac{1}{2}N_1\pi)], \qquad (3.3)$$

where $\mathbf{P}_n$ denotes the totality of $2\pi m$'s and E:

$$\mathbf{P}_n \equiv (2\pi n, E). \qquad (3.4)$$

$F_2^\gamma(\mathbf{q}, \mathbf{P}_n)$ is given by

$$F_2^\gamma(\mathbf{q}, \mathbf{P}_n) = \int_{B_1(R_1)}^{\mathbf{q}} \mathbf{p}_\gamma \, d\mathbf{q} + p_{R,1} R_1, \qquad (3.5)$$

where the + and − signs in (3.3) are for γ equal to II and IV, respectively. At large R in this incident channel p_R is a constant $p_{R,1}$ and equals $-k_n$ (since $\hbar = 1$) and so the F_2^γ given by (3.5) and (3.3) equals

$$F_2^\gamma(\mathbf{q}, \mathbf{P}_n) = \int_{B_1(R_1)}^{\mathbf{q}} p_\gamma \, dq - k_n R \quad (\text{large } R;\ p_R < 0). \qquad (3.6)$$

The part of the wavefunction associated with the outgoing particles $\psi_f(\mathbf{q}, nE)$ is given by a similar expression, but now p_R at large R is positive and so γ is I or III when R is in a reactants' channel. The reflection at small R results in an additional phase loss of $\frac{1}{2}\pi$. Thus, we have

$$\psi_f(\mathbf{q}, nE) = 2^{-1/2} \sum_{\gamma=\mathrm{I,III}} \left| \partial^2 F_2^\gamma / \partial \mathbf{q} \, \partial \mathbf{P}_n \right|^{1/2} \times \exp[i(F_2^\gamma \pm \tfrac{1}{4}\pi - \tfrac{1}{2}N_f\pi - \tfrac{1}{2}\pi)] \quad (R \text{ in reactants' channel}), \qquad (3.7)$$

where the + and − signs are for γ equal to III and I, respectively. N_f is the number of reflections of the trajectory from caustics, apart from the one at small R already included in (3.7).

When R is in the products' channel, the system has not necessarily undergone a reflection at small R, and so the extra $-\frac{1}{2}\pi$ can be absent at Eq. (3.7) in this case.

The wavefunction for the collision $\psi^{(+)}(\mathbf{q}, nE)$ is

$$\psi^{(+)}(\mathbf{q}, nE) = \psi_i(\mathbf{q}, nE) + \psi_f(\mathbf{q}, nE). \qquad (3.8)$$

We comment briefly on the pictorial description of the trajectories in the branches. That for branches II and IV has already been given [Fig. 1(a)]. For branches II and IV at large R all trajectories relevant to $\langle \mathbf{q} \,|\, nE^{(+)} \rangle$ are precollision trajectories and so have the same amplitude. However, for branches I and III at large R the trajectories are postcollision trajectories and so have different amplitudes; they are associated with different final internal energies of the system. Thus, sufficiently adjacent trajectories will still intersect at turning-point surfaces (caustics) but now each caustic surface is no longer, in the example of Fig. 1, a straight line [Fig. 1(a)], but rather is curved, as indicated crudely and incompletely in Fig. 1(b). For *each* trajectory of branch I or III in the postcollision region one can nevertheless still find a point, which we designate as $B_2(R_2)$ at any given R_2, where the p_γ for each now separable internal coordinate would vanish if that internal motion was allowed to occur alone at that R_2. This $B_2(R_2)$ is used later to define a generating function G_2^γ given by Eq. (4.4). $B_2(R_2)$ varies from trajectory to trajectory in this postcollision region because the amplitude of the internal motion is different for the different trajectories.

We note, incidentally, that the trajectories

usually occur in pairs in which p_{II} for one member of the pair is opposite in sign to p_{IV} for the other member, at any R [Fig. 1(a)] and similarly (and as a result) in which p_I for one member is opposite in sign to p_{III} for the other [Fig. 1(b)]. This behavior is responsible for the fact that there are usually two stationary phase points of the integrand in (1.2) for each final internal state, for a system with one internal degree of freedom (2^N for N internal degrees of freedom).

IV. CANONICAL TRANSFORMATION OF COORDINATES AND UNITARY TRANSFORMATION OF $\langle q \mid nE^{(+)}\rangle$

As noted in the introductory section, we shall seek a transformation of coordinates to coordinates in which the usual crossings of adjacent trajectories have been removed. A simple coordinate transformation would not suffice, since such properties of the trajectories are invariant by the latter. Instead, one needs a more general transformation, namely a canonical transformation, in which, therefore, the new coordinates are expressed as functions of both the old coordinates and the old momenta. We employ a canonical transformation in which all but one of the new coordinates describing a point on any trajectory are now constants of the motion and in which the remaining coordinate is, apart from an additive constant, time.

A canonical transformation of coordinates from $\mathbf{q}$ to $\mathbf{Q}$ also gives rise, at the same time, to a unitary transformation of the semiclassical wavefunction, from $\langle q \mid nE^{(+)}\rangle$ to $\langle \mathbf{Q} \mid nE^{(+)}\rangle$ and from $\langle q \mid mE'^{(-)}\rangle$ to $\langle \mathbf{Q} \mid mE'^{(-)}\rangle$. The relation between canonical transformations of coordinates and unitary transformations of semiclassical wavefunctions has been discussed by several authors.[8] The change of the phase and of the pre-exponential factor in the semiclassical wavefunctions is described in the following way [cf. particularly, Eqs. (4.2) and (4.3) below].

If the phase of the original and transformed wavefunctions are $F_2(\mathbf{q}, \mathbf{P}_n)$ and $\bar{F}_2(\mathbf{Q}, \mathbf{P}_n)$ and if $G_1(\mathbf{q}, \mathbf{Q})$ is the generating function for the canonical transformation from $(\mathbf{q}, \mathbf{p})$ to $(\mathbf{Q}, \mathbf{P})$, the former are linked by the usual classical relation,[9]

$$\bar{F}_2(\mathbf{Q}, \mathbf{P}_n) = F_2(\mathbf{q}, \mathbf{P}_n) - G_1(\mathbf{q}, \mathbf{Q}). \tag{4.1}$$

[Equation (4.1) is obeyed since the F_2's and $\bar{F}_2$'s satisfy a Hamilton–Jacobi equation, and hence are generating functions, for transforming from $\mathbf{Q}$, $\mathbf{P}$ or $\mathbf{q}$, $\mathbf{p}$ to $\mathbf{Q}_n$, $\mathbf{P}_n$.[9]] When, as the in the present case, the generating function is given as a function of old coordinates and new momenta $G_2(\mathbf{q}, \mathbf{P}_n)$ then from the standard relation between G_1 and G_2 we have

$$\bar{F}_2(\mathbf{Q}, \mathbf{P}_n) = F_2(\mathbf{q}, \mathbf{P}_n) - G_2(\mathbf{q}, \mathbf{P}) + \mathbf{QP}. \tag{4.2}$$

The relation between the new and the old pre-exponential factors is[8b]

$$\begin{aligned} &\left| \partial^2 \bar{F}_2 / \partial \mathbf{Q}\, \partial \mathbf{P}_n \right|^{1/2} \\ &= \left| \partial^2 F_2 / \partial \mathbf{q}\, \partial \mathbf{P}_n \right|^{1/2} \left| \partial^2 G_1 / \partial \mathbf{q}\, \partial \mathbf{Q} \right|^{-1/2} \\ &= \left| \partial^2 F_2 / \partial \mathbf{q}\, \partial \mathbf{P}_n \right|^{1/2} \left| \partial^2 G_2 / \partial \mathbf{q}\, \partial \mathbf{P} \right|^{-1/2}. \end{aligned} \tag{4.3}$$

In all of the above we have not specified which generating function G_2 we shall use. Equations (4.1)–(4.3) are valid for any choice of G_2. However, in order that the new coordinates $\mathbf{Q}$ have the property that all but one are constants and that the remaining one is time, we choose for G_2 a multivalued solution of the Hamilton–Jacobi equation (2.2). Such a G_2 will be seen below [cf. Eq. (4.9)] to lead to new coordinates $\mathbf{Q}$ with this desired property. G_2^γ is used for branch γ and is calculated relative to a vibrational turning point $B_2(R_2)$ in an outgoing channel at large R, R_2:

$$G_2^\gamma(\mathbf{q}, \mathbf{P}) = \int_{B_2(R_2)}^{q_2(R_2)} p_\gamma\, dq + \int_{q_2}^{\mathbf{q}} \mathbf{p}_\gamma\, d\mathbf{q} + p_{R,2} R_2 \pm \tfrac{1}{4}\pi, \tag{4.4}$$

where $p_{R,2}$ is the final value of p_R on this trajectory passing through $\mathbf{q}$. The integration from B_2 to q_2 is at fixed R_2 and the integral from q_2 to $\mathbf{q}$ is along a dynamical trajectory. Differentiation confirms that $\partial G_2^\gamma / \partial \mathbf{q}$ equals $\mathbf{p}_\gamma$ as it should. The $+\frac{1}{4}\pi$ or $-\frac{1}{4}\pi$ is used when p_γ at $\mathbf{q}_2$ points toward or away from B_2, respectively. When γ refers to an outgoing reactants' trajectory, one would also include the $-\frac{1}{2}\pi$, included earlier in (3.7).

Since the integration in the right-hand side of (4.4) begins in an exit channel (reactants' or products'), $\mathbf{P}$ describes only quantum numbers appropriate to that exit channel. In contrast, $\mathbf{P}_n$ utilizes only the quantum numbers appropriate to the entrance channel.

The $\mathbf{P}$ in Eq. (4.2) must be chosen so that the right-hand side of (4.2) is independent of $\mathbf{q}$, as implied by the arguments of $\bar{F}_2$ on the left-hand side. Thereby, for all $\mathbf{q}$, $\mathbf{P}$ is chosen so that

$$\partial [F_2^\gamma(\mathbf{q}, \mathbf{P}_n) - G_2^\gamma(\mathbf{q}, \mathbf{P})] / \partial \mathbf{q} = 0 \tag{4.5}$$

and hence so that the $\mathbf{p}_\gamma$ given by $\partial F_2^\gamma(\mathbf{q}, \mathbf{P}_n)/\partial \mathbf{q}$ matches that given by $\partial G_2^\gamma / \partial \mathbf{q}$, for all $\mathbf{q}$. If $\bar{n}_2$ denotes the final n's for this trajectory, comparison of (4.4) with (3.5) and (3.2) shows that the $\mathbf{p}_\gamma$'s are matched by setting

$$\mathbf{P} = \mathbf{P}_{\bar{n}_2} \equiv (2\pi \bar{n}_2, E) \tag{4.6}$$

in (4.2).

With these equations, (4.2) then becomes, on integrating by parts,

$$\bar{F}_{2\gamma}(\mathbf{Q}, \mathbf{P}_n) = -\int_{\mathbf{p}[B_1(R_1)]}^{\mathbf{p}[B_2(R_2)]} \mathbf{q}\, d\mathbf{p}_\gamma + \mathbf{Q}\mathbf{P}_{\bar{n}_2} \mp \tfrac{1}{4}\pi. \tag{4.7}$$

The significance of the $\mathbf{Q}$'s conjugate to the $\mathbf{P}$'s

in (4.6) follows from (4.4) and from the Hamilton–Jacobi equation (2.2) satisfied by G_2^γ; $\mathbf{Q}$ is given by

$$\mathbf{Q} = \partial G_2^\gamma / \partial \mathbf{P}. \tag{4.8}$$

Equation (2.2) implies that the new Hamiltonian $\bar{H}(\mathbf{Q}, \mathbf{P})$ is one of the $\mathbf{P}$'s. Hamiltonian's equations then yield

$$\dot{\mathbf{P}} = \partial \bar{H}/\partial \mathbf{Q} = 0,$$
$$\dot{Q}_E = \partial \bar{H}/\partial E = 1, \quad \dot{Q} = \partial \bar{H}/\partial P = 0 \quad (P \neq E), \tag{4.9}$$

where Q_E is canonically conjugate to E.

Thus, all $\mathbf{Q}$'s but Q_E are constants of the motion for a given $\mathbf{P}(=\mathbf{P}_{\bar{n}_2})$ and hence for a given trajectory. These constant Q's will be denoted by $\bar{w}$. Q_E will be denoted by τ, being a time variable, according to (4.9). Since the $\bar{w}$ calculated from (4.8) and (4.4) is constant for the trajectory, we may obtain this value at any $\mathbf{q}$, and it is convenient to choose $\mathbf{q} = (q_2, R_2)$. At sufficiently large R_2, the frequencies $\nu_0[= \partial H_0/\partial(2\pi\bar{n})]$ are constant, and the equations then yield[10]

$$\bar{w} = \nu_0 \int_{B_2(R_2)}^{q_2(R_2)} (dq/\dot{q}) - \nu_0 (R_2/\dot{R}_2). \tag{4.10}$$

The different branches $\gamma = \mathrm{I}, \mathrm{III}$ will map into different values of $\bar{w}$ in this transformation, since $\bar{w}$ is determined by both q_2 and by the sign of p_γ at R_2. The transformation thereby reduces the number of terms in Eq. (3.7) for ψ_f from two to one in this 2-dimensional system. In an s-dimensional system, the corresponding 2^{s-1} terms in ψ_f that would be present in (3.7) would also be reduced to one.

Further, when R_2 is large, Eqs. (4.4) and (4.8) show that when ψ_i is considered, p_R is negative and so $\tau\,(\equiv Q_E)$ is large and negative. When ψ_f is considered, p_R is positive and so τ is large and positive. Thus, the present transformation serves to condense the four terms in (3.8) (and, in the s dimensional case, 2^s terms) into a single term. The factor of $2^{-1/2}$ in (3.3) and (3.7) now becomes unity because of the nature of the mapping and hence the normalization before and after the transformation: One maps a single q, with two different signs of p, onto two different $\bar{w}$'s. The transformed and appropriately normalized wavefunction $\langle \mathbf{Q} \mid nE^{(+)} \rangle$ is

$$\langle \mathbf{Q} \mid nE^{(+)} \rangle = \left| \partial^2 \bar{F}_2 / \partial \mathbf{Q}\, \partial \mathbf{P}_n \right|^{1/2} \exp i(\bar{F}_2 - N\pi), \tag{4.11}$$

where $\bar{F}_2$ is given by (4.7) and where N is the number of times the trajectory touches the upper caustic between $\mathbf{q}_1$ and $\mathbf{q}_2$. Equation (4.11) includes all four possible cases generated by the $\pm\frac{1}{4}\pi$'s in (3.7) and (4.4).

Noting that $\mathbf{Q}$ denotes the constants $\bar{w}$ and the time variable τ one might expect that apart from the $E\tau$ term present in $\bar{F}_2$ (in $\mathbf{Q}\,\mathbf{P}_{\bar{n}_2}$) the wavefunction $\langle \mathbf{Q} \mid nE^{(+)} \rangle$ is independent of the values of R_1 and R_2 present in $\bar{F}_2$. This independence is confirmed in the Appendix.

As noted earlier $F_2^\gamma(q, P_n)$ can be regarded as a generating function for canonically transforming $(\mathbf{q}, \mathbf{p})$ to $(\mathbf{Q}_n, P_n)$, since it satisfies the Hamilton–Jacobi equation (2.2). The "new" Hamiltonian $\bar{H}$ is seen to be E, which is one of the variables. From Hamilton's equations of motion, $\dot{\mathbf{Q}}_n$ equals $\partial \bar{H}/\partial \mathbf{P}_n$ and so is zero unless the $\mathbf{P}_n$ is E, in which case the corresponding $\dot{\mathbf{Q}}_n$ is unity, and so this $\dot{\mathbf{Q}}_n$ is a time variable. Since the other $\mathbf{Q}_n$'s are seen to be constants, they will be denoted by $\bar{w}^0$ and can be evaluated via

$$\bar{w}^0 = Q_n = \partial F_2^\gamma / \partial P_n \quad (P_n = 2\pi n) \tag{4.12}$$

at any $\mathbf{q}$. It is convenient to choose a $\mathbf{q}$ at large R, namely R_1, and so find from (3.6)[10]

$$\bar{w}^0 = \nu_0 \int_{B_1(R_1)}^{q_1(R_1)} (dq/\dot{q}) - \nu_0 R_1/\dot{R}_1. \tag{4.13}$$

These $\bar{w}^0$'s clearly differ from $\bar{w}$'s, as one sees by comparison with (4.11). The $\bar{w}^0$'s and the $\bar{w}$'s are the same as those in Paper III.

Finally, since $\mathbf{Q}_n$ equals $\partial F_2^\gamma/\partial \mathbf{P}_n$ and thence from (4.2) equals $\partial \bar{F}_1/\partial \mathbf{P}_n$, the pre-exponential factor in (4.11) can be rewritten to yield

$$\langle \mathbf{Q} \mid nE^{(+)} \rangle = \left| \partial \mathbf{Q}_n / \partial \mathbf{Q} \right|^{1/2} \exp i(\bar{F}_2 - N\pi). \tag{4.14}$$

V. TIME-REVERSED WAVEFUNCTION $\langle \mathbf{q} \mid nE'^{(-)} \rangle$ AND $\langle \mathbf{Q} \mid mE'^{(-)} \rangle$

The wavefunction $\langle \mathbf{q} \mid mE'^{(-)} \rangle$, where mE' denotes properties for an exit channel, is obtained from $\langle \mathbf{q} \mid mE'^{(+)} \rangle$ by time reversal. The latter can, in turn, be obtained from the arguments in Sec. III, noting only that the roles of R_1 and R_2 are interchanged, since mE' refers to the exit channel. Thereby, we may write

$$\langle \mathbf{q} \mid mE'^{(+)} \rangle = \psi_{i,m} + \psi_{f,m}, \tag{5.1}$$

where, by analogy with (3.3),

$$\psi_{i,m} = 2^{-1/2} \sum_\gamma \left| \partial^2 F_2(\mathbf{q}, \mathbf{P}_m)/\partial \mathbf{q}\, \partial \mathbf{P}_m \right|^{-1/2} \times \exp i[F_2^\gamma(\mathbf{q}, \mathbf{P}_m) \pm \tfrac{1}{4}\pi - \tfrac{1}{2} N_{im}\pi], \tag{5.2}$$

where now

$$F_2^\gamma(\mathbf{q}, \mathbf{P}_m) = \int_{B_2(R_2)}^{\mathbf{q}} \mathbf{p}_\gamma d\mathbf{q} - k_m R_2$$
$$\equiv \int_{B_2(R_2)}^{q_2(R_2)} p_\gamma dq + \int_{\mathbf{q}_2}^{\mathbf{q}} \mathbf{p}_\gamma d\mathbf{q} - k_m R_2 \tag{5.3}$$

and N_{im} is the number of times the trajectory touches a caustic between $\mathbf{q}_2$ and $\mathbf{q}$. The γ's in (5.2) are those corresponding to ingoing particles. $\mathbf{P}_m$ denotes

$$\mathbf{P}_m \equiv (2\pi m, E'). \tag{5.4}$$

Once again, $\psi_{f,m}$ is given by an expression similar to (5.2), apart from an extra $-\frac{1}{2}\pi$ in the phase, when both R_1 and R_2 are in a reactants' channel, and use of appropriate γ's.

$\langle q \mid mE'^{(-)}\rangle$ is obtained from the above equations by reversing the signs of all momenta. The sign of p_R in the $\psi_{i,m}$ contribution to $\langle q \mid mE'^{(-)}\rangle$ is thereby the same as that in the ψ_f contribution $\langle q \mid nE^{(+)}\rangle$ and similar remarks apply to $\psi_{f,m}$ and ψ_i. Thus, when the transformation to $\overline{w}\tau$ is made, the transformed phases in each of these pairs will still be paired, since they will each have the same set of values of τ.

The transformation of $\langle \mathbf{q} \mid mE'^{(-)}\rangle$ using the generating function G_2^γ given by (4.4) yields

$$\langle \mathbf{Q} \mid mE'^{(-)}\rangle = \exp i\mathbf{Q}\,\mathbf{P}_m\,, \tag{5.5}$$

all other terms in $F_2 - G_2$ cancel, since the integrations in this F_2 and G_2 both begin at $B_2(R_2)$ in an exit channel.

VI. S MATRIX

From (1.1) we have

$$S_{mn}\delta(E-E') = \int \langle mE'^{(-)} \mid \mathbf{Q}\rangle d\mathbf{Q}\langle \mathbf{Q} \mid nE^{(+)}\rangle\,. \tag{6.1}$$

Equations (1.1) and (6.1) presume that the state functions have $|nE^{(+)}\rangle$ and $|mE'^{(-)}\rangle$ are normalized to $\delta(E-E')\delta_{nn'}$. In the present case, the wavefunctions (4.14) and (5.5) were normalized to $2\pi\delta(E-E')\,\delta(n-n')$, and so should be multiplied by $(2\pi)^{-1/2}$. These equations and (6.1) then yield, on integration over Q_E, i.e., over τ, a factor which cancels the δ function (we use real τ, as discussed below) and which leaves

$$S_{mn} = \int \mid \partial\overline{w}^0/\partial\overline{w} \mid^{1/2} \exp i(\overline{F}_4 - N\pi)\,d\overline{w}, \tag{6.2}$$

where

$$\overline{F}_4 \equiv -\int_{\mathfrak{p}(B_1)}^{\mathfrak{p}(B_2)} \mathbf{q}\,d\mathbf{p} + 2\pi(\overline{n}_2 - m)\overline{w}. \tag{6.3}$$

$\overline{w}$ is defined by (4.11) and N was defined immediately after (4.14). The integral in (6.2) can be transformed into one over $\overline{w}_0$:

$$S_{mn} = \int_{\overline{w}_0=0}^{1} \mid \partial\overline{w}/\partial\overline{w}^0 \mid^{1/2} \exp i(\overline{F}_4 - N\pi)\,d\overline{w}^0 \tag{6.4}$$

and $\overline{w}^0$ varies from 0 to 1.

In the Appendix, it is shown that (4.14), (5.5), and (6.4) are independent of the choice for R_1 and R_2. Further, in obtaining (6.2) from (6.1) real τ was used, i.e., systems were treated where products were reached from reactants without tunneling.

VII. EXTENSION TO HIGHER NUMBER OF DIMENSIONS

When the number of coordinates is greater than two, the phase of the unperturbed wavefunction at large R, $F_2^0(\mathbf{q}, \mathbf{P}_n)$, can be written as

$$F_2^0(\mathbf{q}, \mathbf{P}_n) = F_1^0(\mathbf{q}, \mathbf{q}_1) + f_2(\mathbf{q}_1, \mathbf{P}_n)\,,$$

where F_1^0 is a phase integral $\int \mathbf{p}d\mathbf{q}$, integrated from $\mathbf{q}_1$ to $\mathbf{q}$, $\mathbf{P}_n$ denotes the quantum numbers and energy as in (3.4), and f_2 is a standard generating function[11] for transforming the conventional internal coordinates $\mathbf{q}_1$ to action variables [the latter equal $(n_i+\delta_i)h$ or in units of $\hbar = 1$, $2\pi(n_i+\delta_i)$]. A vibration contributes to f_2 the term $\int p\,dq$, integrated from vibrational turning point $B_1(R_1)$ to $\mathbf{q}_1$. The radial, orientational, and polar coordinates also contribute to f_2 by a standard expression,[11] which we shall denote by $f_2^\alpha(\mathbf{q}_1, \mathbf{P}_n) + p_{R_1}R_1$. In the system of Sec. II $f_2(\mathbf{q}_1, \mathbf{P}_n)$ was $p_{R_1}R_1$.

Equations (3.2) and (3.7) remain unchanged, but of course $\mathbf{p}_\gamma d\mathbf{q}$ denotes a sum of terms, as does $p_\gamma dq$. Equation (3.3) again applies, except for a modification of the $\pi/4$ terms as discussed below. Equations (3.5) and (3.6) again follow, but now the right-hand side also contains the term $f_2^\alpha(\mathbf{q}_1, \mathbf{P}_n)$. Equations (4.1)–(4.3) are unaffected. The right-hand side of (4.4) contains additional $\pm\frac{1}{4}\pi$ terms (discussed below) and $f_2^\alpha(\mathbf{q}_2, \mathbf{P})$. Equation (4.7) is unaffected apart from the $\mp\frac{1}{4}\pi$ terms. The expression (4.8) for $\mathbf{Q}$ and hence for $\overline{w}$ yields an angle variable w, minus the last term of (4.10).[10]

The terms in Sec. III involving $\pm\frac{1}{4}\pi$ and N_i [Eq. (3.3)] can also be immediately extended to a higher number of dimensions. For example, for three coordinates ($s=3$), one has instead of the open-ended rectangle in Fig. 1(a) an open-ended box. The edges of the rectangle were the caustics and now the sides of the box form the caustic surfaces. The turning point $B_1(R_1)$ in Eq. (3.2) is now a turning point for both vibrations and so is chosen to lie at the intersection of a preselected two of the four caustic surfaces at a given R_1, which we will call "near caustics." At any other R, this locus of points on this intersection, will be denoted by $B(R)$. One of the two near caustics plays the same role, for one of the internal coordinates, as that played by the lower dotted line in Fig. 1(a) or (b), while the other plays a similar role for the second internal coordinate.

The remaining two caustics surfaces will be called "opposite caustics." One of these plays the same role for one of the internal coordinates as that played by the upper dotted line in Fig. 1(a) or (b) and the second plays a similar role for the other coordinate. The integration in (3.2) from B_1 to q_1 is an integration first over one of the internal coordinates, holding R_1 and the other coordinate fixed, until the desired component of $\mathbf{q}_1$ is reached and then over the second internal coordinate, holding the other two coordinates fixed, until

its desired component of $\mathbf{q}_1$ is also reached. The integral from $\mathbf{q}_1$ to $\mathbf{q}$ in (3.2) is again an integral over a dynamical trajectory.

The sum in (3.3) now has four terms instead of two, the four corresponding to the four possible combinations of signs of the two internal momenta at R_1. The $\pm\frac{1}{4}\pi$ in (3.3) is replaced by $\pm\frac{1}{4}\pi\pm\frac{1}{4}\pi$, the plus signs being used when both internal momenta at R_1 point toward $B_1(R_1)$, the two minus signs are used when they point away form $B_1(R_1)$, and the remaining two sign combinations correspond to the two remaining ones of the p's.[10] The N_i in (3.3) is again the number of times the trajectory touches a caustic surface. The same remarks apply to (3.7), there now being four terms in the latter and the $\pm\frac{1}{4}\pi$ being replaced by $\pm\frac{1}{4}\pi\pm\frac{1}{4}\pi$. Similar remarks apply to (4.4), (4.7), and (5.2). $B_2(R_2)$ is the value of $B(R)$ at $R=R_2$.

One obtains two $\bar{w}$'s one for each of the internal coordinates and each of the form (4.10). One also again obtains (4.11) N now being the number of times the trajectory touches opposite caustics between $\mathbf{q}_1$ and $\mathbf{q}_2$. The equations of Sec. VI again follow.

Similarly, the equations in Sec. VI are obtained for any dimensionality s.

APPENDIX: INDEPENDENCE OF WAVEFUNCTIONS AND EQ. (6.2) ON R_1 AND R_2

It is first shown that $\bar{F}_2-E\tau$ in (4.7),

$$\bar{F}_2^{\gamma}(Q,P_n)=-\int_{\mathfrak{p}[B_1(R_1)]}^{\mathfrak{p}[B_2(R_2)]}\mathbf{q}\,d\mathbf{p}_{\gamma}+\mathbf{Q}\mathbf{P}_{\bar{n}_2}\mp\tfrac{1}{4}\pi, \qquad (4.7)$$

is independent of the choice of R_2. To this end it is useful throughout this Appendix to subdivide a trajectory at large R_2 into R intervals, each interval being bounded by successive R's for which the trajectory touches the upper caustic. Such an interval will simply be called an R interval. The $-\int\mathbf{q}\,d\mathbf{p}$ in (4.7) is independent of the choice of R_2 for all R_2's in this R interval: $-\int R\,dp_R$ makes no contribution since p_R is constant at large R; $-\int q\,dp$ is unchanged, since the upper limit of this integral is always the p at the lower vibrational turning point, regardless of R_2.

If, however, R_2 is in the next R interval of the trajectory at larger R, the contribution $-\int q\,dp$ has increased by an amount equal to its value over one vibrational cycle, namely $\oint p\,dq$, which in turn equals $2\pi(\bar{n}_2+\frac{1}{2})$; $-\int R\,dp_R$ is again unchanged.

The $\bar{w}$ in (4.7) is independent of R_2, as long as R_2 lies in the given R interval: $d\bar{w}$ equals $\nu_0[dq/\dot{q}-dR_2/\dot{R}]$, i.e., $\nu_0(dt-dt)$ or 0. At the boundary between two adjacent R intervals, $\bar{w}$ changes discontinuously by -1 when R_2 is changed from just less than to just greater than the R at the boundary. [The value of $\nu_0\int_{B_2}^{q_2}(dq/\dot{q})$ in (4.10) approaches $+\frac{1}{2}$ or $-\frac{1}{2}$ when q_2 becomes the upper turning point, depending on the sign of $\dot{q}$.] Thus, the $2\pi\bar{n}_2\bar{w}$ in (4.7) is constant in any given R interval but jumps by $-2\pi\bar{n}_2$ when R_2 is placed in the adjacent R interval at larger R.

The N in (4.15) is unchanged when R_2 is varied, as long as R_2 remains in the given R interval, but jumps by unity when R_2 is placed in the adjacent R interval at larger R.

Thus, as long as R_2 remains in a given R interval, (4.7) shows that $\bar{F}_2-E\tau$ remains unchanged. When R_2 is placed in the next R interval at larger R, $\bar{F}_2-E\tau$ changes by $2\pi(\bar{n}_2+\frac{1}{2})-2\pi\bar{n}_2-\pi$, from the above arguments. Thus, it too remains unchanged. Similar remarks apply to changes of R_2 to any other R intervals at still larger R_2. The pre-exponential factor in Eq. (4.14) is also unchanged, it being equal to $|\partial\bar{w}/\partial\bar{w}^0|^{1/2}$.

We consider next the effect of a change of R_1 on $\bar{F}_2-E\tau$. This time $\bar{w}$ is unaffected, since its definition involves only R_2. $-\int R\,dp_R$ is of course unaltered; $-\int q\,dp$ is unchanged as long as R_1 lies in a given R interval, but increases by $\oint p\,dq$, i.e., by $2\pi(n+\frac{1}{2})$, when R_1 is placed in the adjacent R interval at larger R_1. N also stays constant in a given R interval and increases by unity when R_1 is in the adjacent interval at larger R. Thus, a change in R_1 either causes $\bar{F}_2-E\tau$ to remain constant or, when R_1 is placed in the adjacent R interval at larger R to increase by $2\pi n$, a change which leaves $\exp i(\bar{F}_2-E\tau)$ unaltered.

Again, if one considers the $2\pi m\bar{w}$ in the exponent $\mathbf{Q}\mathbf{P}_m$ in Eq. (5.5) for $\langle\mathbf{Q}\,|\,mE'^{(-)}\rangle$, $\bar{w}$ remains constant in a given R interval but changes by unity when R_2 is placed in an adjacent R interval. However, the $\exp 2\pi im\bar{w}$ in $\langle\mathbf{Q}\,|\,mE'^{(-)}\rangle$ changes only by $\exp 2\pi im$ and hence is unaffected, m being an integer.

From these arguments one also sees that the integrand in (6.2) is also unchanged when R_1 or R_2 are altered.

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[6]For example J. B. Keller, Ann. Phys. (N.Y.) **4**, 180 (1958).

[7]One can show that these normalizations are equivalent by actual calculation.

[8](a) V. A. Fock, Vestn. Leningr. Univ. Ser. Fiz. Khim. **16,** 67 (1959) [Tech. Transl. **4**, No. 60–17464 (1960)]; (b) R. Schiller, Phys. Rev. **125,** 1109 (1962); (c) W. H. Miller, J. Chem. Phys. **53,** 1949 (1970).

[9]For example, H. C. Corben and P. Stehle, *Classical Mechanics* (Wiley, New York, 1960), 2nd ed., p. 251, Eq. (76.3).

[10]For some degrees of freedom q' there is no turning point at large R_2. For those the q' component of B_2 is chosen to be any preassigned value, and the $\pm (1/4)\pi$ terms in (3.3) and in subsequent equations are absent. For some degrees of freedom, too, the result obtained for $\bar{w}$ from (4.8) and (4.4) is more complicated than (4.10), but, as comparison with the standard definition (Ref. 9, p. 188) of an angle variable w shows, $\bar{w}$ still equals w, defined over a unit interval, minus the last term in (4.10). As such, it has the properties used in the Appendix.

[11]L. A. Pars, *Analytical Dynamics* (Wiley, New York, 1965), pp. 573–603.